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FLAMEPROOFING OF COTTON WITH THPC-RESINS[1]

by

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Efforts to develop better flame-resistant finishes for textiles have been intensified because of increased general interest in safety. Some of the currently available methods for flameproofing fabrics depend on the use of water-soluble salts which must be renewed after each laundering, while other available methods, although they impart flame resistance having various degrees of fastness to washing, are not entirely satisfactory due to adverse effects on fabric properties or to high cost.

The importance of flameproofing certain kinds of fabrics used in garments is brought out by an article by Colebrook (1) which states that from the beginning of 1945 to the end of 1950, 263 people were hospitalized in Birmingham, England, a city of 1.2 million, due to ignition of their clothing and 62 of these died. It may be estimated from Colebrook's data that about 1250 people in the United States die and several thousand more are injured each year due to burning clothing. Legislators have realized the seriousness of flammable textiles and the 83rd Congress enacted Public Law 88, entitled "Flammable Fabrics Act" (2) to prohibit the introduction or movement in interstate commerce of articles of wearing apparel and fabrics which are so highly flammable as to be dangerous when worn by individuals.

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[1] The work on developing this process was supported in part by the Quartermaster Corps.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Services, U. S. Department of Agriculture.

According to Buck (3), fire-retardant finishes for textiles are applied at present almost exclusively to cotton and rayon. These goods are finished for outdoor uses, such as tents, awnings, tarpaulins, truck and boat covers, and other special-purpose protective fabrics for both military and civilian use; and for indoor uses, such as curtains, drapes, upholstery, and a few special types of clothing such as welders' and steel workers' coveralls and fire fighters' clothing. Because of the great need for a better, durable type, flame-retardant finish suitable for many end uses, work was undertaken to develop such a finish for cotton fabrics.

Numerous approaches to the problem were tried, but the first lead to the method described in this paper was obtained, during the investigations of the chemical properties of aminized cotton (4), when it was found that tetrakis-(hydroxymethyl)phosphonium chloride would react with an make aminized cotton fabric flame-resistant. When an aqueous solution of tetrakis(hydroxymethyl)-phosphonium chloride, $(HOCH_2)_4PCl$, abbreviated THPC, was padded on aminized cotton and dried, the phosphorus compound combined with the amino groups of the modified cotton in such a manner that it was very stable to boiling sodium hydroxide solutions.

In order to flameproof cotton without having to start with aminization the reaction of THPC and polyfunctional monomeric amines like melamine was studied. From this work it was found that permanent flame-resistance could be imparted to cotton fabric by treating it with a solution containing THPC, methylolmelamine, and other substances, followed by drying and curing. The THPC polymerizes with the methylolmelamine to form an insoluble resin inside the cotton fibers.

Description of the Flameproofing Process

Chemicals used. A typical resin-forming flameproofing solution contains 15.8 percent THPC, 9.5 percent trimethylolmelamine (Resloom HP[3/]), 9.9 percent urea, and 3.0% triethanolamine. The THPC is a crystalline compound that is soluble in water and in many organic solvents including alcohols and pyridine. It is made by reacting phosphine with aqueous hydrochloric acid and formaldehyde (5). Until just recently this compound was not available, even in small quantities from any known source, but as a result of current interest in its possible use as a flameproofing agent, it is now being made on a pilot plant scale by at least one company.

Methylolmelamines are made by reacting formaldehyde with melamine (6). These melamine derivatives may contain from one to six methylol groups, depending upon the amount of formaldehyde reacted with the melamine. Any of these methylolmelamines, and melamine itself, form polymers with THPC, but due to differences in water solubility and in other properties some are more desirable in flameproofing formulations than others. They become more water-soluble as the number of methylol groups increases. Trimethylolmelamine has been found to be very satisfactory in the typical formultion given above. Trimethylolmelamines as sold commercially are actually mixtures of methylolmelamines that have an average of approximately three methylol groups per molecule. For this and other reasons the trimethylolmelamines purchased under different trade names may differ somewhat in solubility or other properties. Methylol ureas can be substituted for the methylolmelamine but when this is done modifications must be made in formulations and processing.

During polymerization, hydrochloric acid is split out of the THPC molecule. Hence urea is employed in the formulation primarily to tie-up this free acid formed during the curing operation in order to protect the cotton from acid

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[3/] This name is given for convenience only and is not to be construed to be a recommendation by the U. S. Department of Agriculture over equivalent products of other companies. Equivalent products may be used if suitable modifications in amounts and processing conditions are made.

tendering. Even though the minimum amount of urea needed to prevent acid tendering is associated with the amount of THPC in the formulation, it is difficult to calculate the amount of urea to use because some of the urea actually reacts with THPC to become part of the polymer and some of it decomposes during the high temperature cure. The amount of urea needed has been established experimentally, and the effects of varying the concentration of urea in the typical formulation have been determined by curing the resin in 8 oz. twill. Fabric treated with resin-forming solutions which contained no urea picked up only about 12 percent resin and was tendered, according to tear strength measurements. As the urea concentration was raised to about 10 percent, the resin pickup increased to about 17 percent, and there was little loss in tear strength. Twenty-five percent urea prevented tendering but this amount interfered with the polymerization of THPC and methylolmelamine to the extent that only about 5 percent resin was deposited in the fabric. Some experiments have indicated that use of about 7.5 percent urea instead of the 9.9 percent given above in the typical formula will give somewhat better permanence to laundering with soap and soda.

The triethanolamine also plays an important role in the resin-forming solution. A water solution of THPC, trimethylolmelamine, and urea, all in concentrations referred to above as representing a typical solution, will polymerize to a viscous liquid or even gel within a few hours at room temperature; and the use of such a viscous solution tends to cause fabric stiffness. Triethanolamine is used to stabilize the resin-forming solution at room temperature and less than 1 percent of triethanolamine retards polymerization, while 4 percent will stabilize solutions for several hours. THPC-trimethylolmelamine solutions are reasonably stable at pH 7, but the rate of polymerization increases as the pH falls to about 5 or 6. Amounts of triethanolamine somewhat greater than suggested do not affect the quality of the flameproofed goods.

If grey goods are processed, a wetting agent must be incorporated in the resin-forming solution in order to wet-out the material; it might actually be advantageous to include about 1 percent of a wetting agent, like Triton X-100[3/], in the solution when treating fabrics other than grey goods.

Processing. Fabric can be processed on a continuous basis or it can be processed step-wise. In either case it is padded in the resin-forming solution, dried, cured, washed, softened, and then dried.

In general, fabric will receive a more uniform application if it is padded through the resin-forming solution twice using a very tight squeeze roll setting each time. To prevent solution migration, and stiffening of the treated goods, only moderate tension should be applied to the fabric as it comes from the padder and it should be dried as soon as possible at a temperature of about 185° F. Drying temperatures above about 220° F. cause surface curing before the inside of the yarn is dry. The length of time fabric is dried is not critical except that it must be dry before resin-curing begins.

It is necessary that the THPC-resin be cured at an elevated temperature in order to fix it in the fiber. The temperature of the cure is dependent upon length of time cured. A short cure time requires a high temperature and vice versa. The preferred temperature and time of cure will vary for different materials. Eight ounce twill is adequately cured in about 4.5 minutes at 285° F. Much shorter times than this at the same temperature reduce the efficiency of the resin-forming solution but, fortunately, little or no harm is done if the fabric is cured twice as long. The effects of prolonged cure times at temperatures above 285° F. are not yet known. The curing oven should be well vented. The possible toxicity of the fumes evolved during curing has not been investigated. Excess salts can be washed from the cured goods by almost any technique since they

are water-soluble and a softener can be applied during the last rinse. Although the resin treatment does not lower the breaking strength, it generally reduces the tear strength, but if a softener, like Triton X-400[3] is applied after the resin treatment, the tear strength is usually equal to that of the untreated fabric and this relationship is maintained through many launderings.

The THPC treatment is compatible with water repellent treatments. Some of these act as softeners and improve the hand and tear strength. They may be applied after the flameproofing treatment or, in some cases, may be incorporated into the flameproofing solution and applied in one padding and curing operation.

The amount or degree of flameproofing is dependent upon the amount of resin put into the fabrics and upon fabric construction. Only about 10 percent resin is required to flameproof 32 oz. duck belting so that it will pass the standard vertical test (Fed. Spec. CCC-T-191b), whereas, about 16 percent is required for 8 oz. twill and about 32 percent for 2 oz. marquisette. The minimum amount of resin that will flameproof a particular piece of goods can be established by a few preliminary experiments. The amount of resin introduced into a piece of material can be varied by merely varying the concentration of the reagents in the resin-forming solution.

The process is illustrated by the following description of a typical laboratory-scale application to 8 oz. cotton twill.

A. Preparation of solution:

(1) 1868 g. of crystalline THPC (purity 95%) were dissolved in 1800 g. of water, then 338 g. of triethanolamine were added.

(2) 1069 g. of trimethylolmelamine (unmethylated) and 1114 g. of urea were dissolved in 5062 g. of water. In this particular experiment the trimethylolmelamine was the trade product, Resloom HP[3].

Both solutions should be made at room temperature and heat should not be applied to the solutions before they are padded on fabric.

B. Padding:

Solutions (1) and (2) were mixed and 100 yards of 18 inch wide 8 oz. O.D. twill was padded using 2 dips and 2 nips with a tight squeeze roll setting. The wet pickup was 71.5%.

C. Drying:

The fabric was dried 4.5 minutes by passing it through a forced draft oven at 185° F.

D. Curing:

The fabric was cured 4.5 minutes by passing it through a forced draft oven at 285° F.

E. Washing and Drying:

The fabric was washed in a winch, first in cold water, then in hot water containing 0.1% Duponol LS[3/] (flakes) and then rinsed in water. It was dried by passing it through the oven.

F. Softening:

The dried fabric was softened by padding with a 4 percent solution of a cationic softener to a 50 percent pickup. In this particular experiment, the cationic softener was the trade product, Triton X-400[3/]

The above example is illustrative only, since the amount of resin add-on and curing conditions may have to be varied according to the type of fabric and degree of flame resistance required. It is suggested that mill trials be preceded by laboratory experimentation on the particular fabric to be flameproofed. In general, the curing conditions used for the crease-proofing resins should be satisfactory.

Properties of the Flameproofed Fabrics

Fabrics flameproofed at this Laboratory with the above typical formulation passed the standard vertical test after 15 launderings with Igepon T[3] followed by a laundry sour in accordance with Federal Specification CCC-T-191b. Little or no loss of resin, based on phosphorus and nitrogen analyses, is observed during such washes. However, some applications of the above formulation show about 15 percent loss of resin on boiling in soap and soda solutions for 3 hours. Permanence of the flameproofing to such treatments may be obtained by greater original resin add-on or by decreasing the amount of urea in the treating solution. Use of 7.5 percent urea instead of the 9.9 percent given in the typical formulation is suggested.

Resin pickup as low as 13 percent imparts sufficient flame resistance to 8 oz. twill so that it will pass the standard vertical flame test, but about 16 percent resin is recommended to give it greater flame resistance. This 16 percent pickup is considerably less than is required with most permanent type flameproofing agents some of which require up to 50 percent pickup to provide adequate flame resistance.

A very important property of materials flameproofed with THPC-resins is that the goods are also glowproof. The glow that usually persists after the flame of burning cotton is extinguished, often completely consumes the fabric. The afterglow of THPC-resin-treated 8 oz. twill lasts less than two seconds.

Many resin treatments, especially the urea-formaldehyde resins, reduce both the tear and breaking strength of cotton fabrics by about 35 percent when about 15 percent of the resins is put on the goods. The THPC-resins have very little effect upon the breaking strength but do, in general, reduce the tear strength somewhat. The loss in tear strength depends on the kind of fabric, a very tightly woven fabric being apt to lose more tear strength than a loosely constructed material. The application of a softener to THPC-resin-treated fabric

brings back the tear strength of almost any fabric to about equal that of the untreated goods. In some cases the tear strength of THPC-resin-treated goods, with softener, has been even greater than that of the untreated fabric.

Fabrics flameproofed with THPC-resins show improved crease-resistance, often as much as 30 percent as measured by the usual tests. This property may be of value in certain uses, especially in clothing. There is also some evidence that the treatment imparts considerable resistance to shrinkage. While the extensive work done with THPC and THPC-resins has not suggested any hazards involved in handling and applying these materials, adequate tests for toxicity and skin irritation have not yet been made.

For uses such as tentage materials and awnings, flameproofed goods are often treated with a mildew- or rot-proofing agent to protect them from micro-organisms. Such an after-treatment may not be necessary for goods flameproofed with THPC-resins because the resin itself protects the materials. Some THPC-treated 8 oz. fabric has been exposed to rain and sunshine for three months in a warm humid climate without any visible mildew formation. In this same experiment, untreated fabric contained a considerable amount of mildew in three months. These samples are still under observation. The soil burial test has been used as an accelerated method of determining the resistance to micro-organisms of fabrics treated with THPC-resins. Samples have retained 85 percent breaking strength after 112 days in the soil, whereas untreated 8 oz. twill retained only 3 percent strength after 10 days.

Summary

A rather unusual chemical compound has been found which can be applied in combination with other chemicals to cotton fabric to make it permanently flame-resistant. This crystalline compound is tetrakis(hydroxymethyl)phosphonium chloride, $(HOCH_2)_4PCl$, abbreviated "THPC".

The flameproofing treatment can be applied on standard chemical finishing equipment. An aqueous solution of THPC, trimethylolmelamine, urea, and triethanolamine is applied to fabric with a padder with a tight nip roll pressure to keep the wet pickup at a minimum. The fabric is then dried at a relatively low temperature, cured at an elevated temperature, and washed by any of the usual washing procedures. A softener should be applied to the treated fabric.

Eight ounce twill containing about 16 percent of the THPC-resin will pass the standard vertical flame test. The resin is permanent to laundering. In addition to being flameproof, treated fabric is also glowproof. Considerable wrinkle resistance and rot or mildew resistance are imparted by the flameproofing treatment.

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